(C-3), 116.5 (CN), 132.3 (C-4), 136.4 (C-2), 141.2 (C-1) ppm.

3-Cyano-5-nitrotoluene (2e). 4-Methyl-2-nitroaniline was brominated in glacial acetic acid to give 2-bromo-4-methyl-6-nitroaniline in 85% yield, mp 62–63.5 °C (lit.[15] mp 64.5 °C), which was then deaminated as above to give 3-bromo-5-nitrotoluene in 90% yield, yellow crystals, mp 83–84 °C (lit.[25] mp 83 °C). A modified Rosenmund–von Braun reaction using cuprous cyanide in dry pyridine was then used to convert 3-bromo-5-nitrotoluene into 3-cyano-5-nitrotoluene in 58% yield, yellow needles, mp 104–105 °C (lit.[16] mp 104.5 °C).

Benzylic Brominations. Each of the 5-substituted 3-cyanotoluenes **2** was individually brominated by overnight reflux of a carbon tetrachloride solution of equimolar amounts of toluene and NBS with a catalytic amount of 2,2′-azobisisobutyronitrile. The resulting solution was filtered hot, the solvent was removed under vacuum, and the product benzyl bromides were purified by recrystallization or column chromatography. The following benzyl bromides were obtained.

α-Bromo-3-cyanotoluene (8a): mp 92–93 °C (lit.[26] mp 93 °C).

3-(Bromomethyl)-5-methylbenzonitrile (8b): mp 92–93 °C (lit.[21] mp 87–88 °C).

α-Bromo-3-bromo-5-cyanotoluene (8c): mp 112–113 °C, after repeated sublimation; IR (KBr) 3060 (ArH), 2237 (CH) cm^{1}; ^1H NMR ($CDCl_3$) δ 4.45 (s, 2 H), 7.6–8.0 (m, 3 H) ppm; MS (70 eV) *m/e* (relative abundance) 277 (5), 275 (10), 273 (6), 196 (100), 194 (98), 115 (46).

Anal. Calcd for $C_8H_5Br_2N$: C, 34.93; H, 1.82; N, 5.09. Found: C, 35.20; H, 1.72; N, 4.92.

α-Bromo-3,5-dicyanotoluene (8d): mp 124–125 °C; separated by column chromatography on silica gel using hexane/toluene; white crystals; IR (KBr) 3062 (ArH), 2243 (CN) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.50 (s, 2 H), 7.94 (s, 3 H) ppm; MS 222 (3), 220 (4), 141 (100), 114 (23).

Anal. Calcd for $C_9H_5BrN_2$: C, 48.49; H, 2.26; N, 12.68. Found: C, 49.10; H, 2.33; N, 12.57.

α-Bromo-3-cyano-5-nitrotoluene (8e): mp 102–103.5 °C; separated by column chromatography on silica gel using petroleum ether; IR (KBr) 3085 (ArH), 2243 (CN), 1543 and 1358 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.60 (s, 2 H), 8.03 (s, 1 H), 8.47 (s, 2 H) ppm; MS 244 (2), 240 (3), 161 (100), 115 (39).

Anal. Calcd for $C_8H_5BrN_2O_2$: C, 39.85; H, 2.08; N, 11.62. Found: C, 40.54; H, 2.34; N, 11.32.

α,α-Dibromo-3,5-dicyanotoluene (9d): mp 118–120 °C; separated from **8d** by column chromatography on silica gel with hexane/toluene; IR (KBr) 3060 (ArH), 2245 (CN) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.73 (s, 1 H), 8.03 (s, 1 H), 8.23 (s, 2 H) ppm; MS 221 (97), 219 (100), 140 (27), 113 (14).

Anal. Calcd for $C_9H_4Br_2N_2$: C, 36.02; H, 1.33; N, 9.34. Found: C, 35.79; H, 1.19; N, 9.15.

α,α-Dibromo-3-cyano-5-nitrotoluene (9e): mp 97–98.5 °C; separated from **8e** by column chromatography on silica gel with 2:1 cyclohexane–toluene; IR (KBr) 2238 (CN), 1555 and 1357 (NO_2) cm^{-1}; $_1H$ NMR ($CDCl_3$) δ 6.80 (s, 1 H), 8.30 (s, 1 H), 8.57 (s, 1 H), 8.77 (s, 1 H) ppm; MS 319 (1), 241 (95), 239 (100), 117 (74).

Anal. Calcd for $C_8H_4Br_2N_2O_2$: C, 30.02; H, 1.25; N, 8.76. Found: C, 29.84; H, 1.11; N, 8.48.

Registry No. **2a**, 104-85-8; **2b**, 22445-42-7; **2c**, 124289-21-0; **2d**, 39718-07-5; **2e**, 124289-22-1; **3**, 2941-78-8; **4**, 13091-43-5; **5** (X = Br), 58530-13-5; **5** (X = Me), 499-06-9; **6**, 89-62-3; **7**, 52488-28-5; **8a**, 28188-41-2; **8b**, 124289-23-2; **8c**, 124289-24-3; **8d**, 124289-25-4; **8e**, 124289-26-5; **9d**, 124289-27-6; **9e**, 124289-28-7; uvitic acid, 499-49-0; 2-bromo-4-methyl-6-nitroaniline, 827-24-7.

(25) Gibson, J. *J. Chem. Soc.* **1924**, 1244.
(26) Braum, J.; Reich, H. *Justus Liebigs Ann. Chem.* **1925**, *445*, 237.

Cumulene Photochemistry: Substituent Effects on the Mechanism of 1,2-Cyclononadiene Photochemistry

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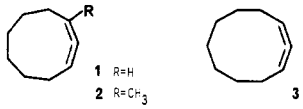
The photoreactions of 1-methyl-1,2-cyclononadiene (**2**) are described and contrasted with those of 1,2-cyclononadiene (**1**). Direct irradiation yields as primary products seven isomers. The major singlet products are best accounted for by excited-state 1,2-hydrogen migration to 3-methylcyclonon-2-enylidene (**15**). Independent generation of this vinylcarbene and an isomeric carbene are reported. Minor products from **2** include 3-methylcyclononyne (**9**) and two isomeric tricyclo[4.3.0.$0^{2,9}$]nonanes (**7** and **8**). An important conclusion is that in contrast to the apparently concerted reaction of **1**, methyl derivative **2** seems to favor vinylcarbene intermediates. Triplet-sensitized reactions of **2** are similar to **1**, affording isomeric tricyclononanes **7** (46%) and **8** (41%).

Introduction

Previous investigations of the solution- and gas-phase photochemistry of 1,2-cyclononadiene (**1**)[1,2] and 1,2-cyclodecadiene (**3**)[3] have demonstrated the diversity of singlet and triplet excited-state reactions of the allene (1,2-propadiene) chromophore.[4] Simple π bond rotation, which interconverts enantiomers, is observed to be the most rapid reaction of optically active **1**[2] in the solution phase. The other dominant singlet reaction of **1** and **3** is 1,2-hydrogen migration, which may be a concerted process. This is accompanied by less efficient 1,3-hydrogen migration and transannular insertion. Vapor-phase triplet reactions of **1** and **3** afford primarily tricyclic isomers, which result from intramolecular hydrogen abstraction.[1-3]



Comparison of the singlet excited state behavior of **1** with reactions of other allenes suggested a close relationship between concerted 1,2-hydrogen migration and rearrangement via vinylcarbene intermediates.[5,6] We describe here the photoreactions of 1-methyl-1,2-cyclo-

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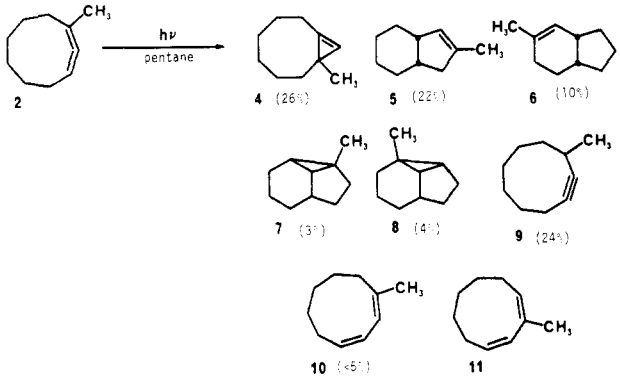
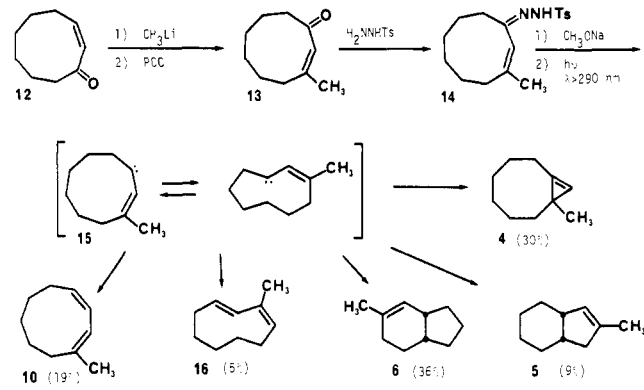
(1) Ward, H. R.; Karafiath, E. *J. Am. Chem. Soc.* **1969**, *91*, 522.
(2) Stierman, T. J.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 3971.
(3) Price, J. D.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 2187.
(4) Reviews: (a) Steinmetz, M. G.; Srinivasan, R.; Leigh, W. J. *Rev. Chem. Intermed.* **1984**, *5*, 57. (b) Johnson, R. P. *Org. Photochem.* **1985**, *7*, 75.
(5) Klett, M. W.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 3963.
(6) Steinmetz, M. G.; Mayes, R. T. *J. Am. Chem. Soc.* **1985**, *107*, 2111.

0022-3263/90/1955-1043$02.50/0

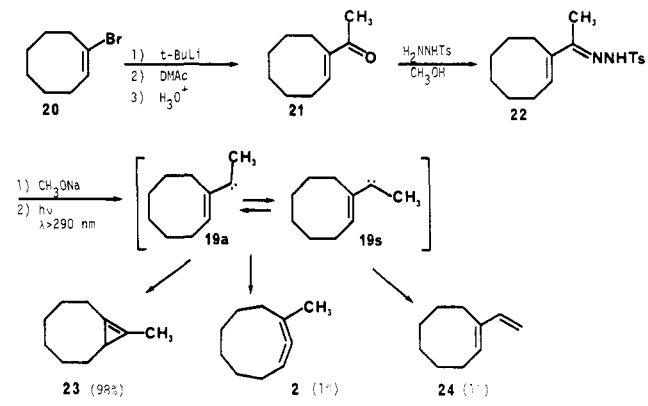
Scheme I



Scheme II



Scheme III



nonadiene (**2**), which show that simple alkyl substitution easily diverts reaction of **1** from a concerted mechanism toward vinylcarbenes.

Exploratory Singlet Photochemistry. 1-Methyl-1,2-cyclononadiene (**2**) was prepared in 98% purity and 94% yield by treatment of the dibromocarbene adduct of 1-methylcyclooctene with methyllithium.[7] Samples for analytical experiments were further purified by preparative GLC.

Irradiation of dilute pentane solutions of GLC purified **2** with wavelengths >220 nm (Vycor filtered 450-W lamp), or at 185 (+254) nm (Rayonett apparatus) yielded the collection of isomeric products shown in Scheme I. With the exception of **10** and **11**, the product distribution, as analyzed by capillary GLC, was essentially constant up to ca. 15% conversion and independent of wavelength. Among these products, **4–9** were clearly primary. Diene **10** also is detectable in the mixture; this undergoes very rapid secondary reactions, and we believe it is a primary product of **1**. Diene **11** is a secondary product of **10**.[8] We estimate that isomers **4–10** comprise >95% of the primary photochemistry of **2**.

The photoproducts were isolated by preparative GLC and identified by spectral data, with comparison to the nonmethylated analogues, or by independent synthesis. Cyclopropene **4** and alkyne **9** both showed IR and NMR data which were characteristic of their functional groups. A sample of **4** was independently prepared (vide infra) by a vinylcarbene route. Authentic samples of bicyclic alkenes **5** and **6** were both independently synthesized from known cis ketone precursors.[9] ^{1}H NMR spectra for methyl-substituted tricyclics **7** and **8** were extremely similar to the parent compound.[2] Dienes **10** and **11** have been previously described.[10] Authentic samples were conveniently prepared by base-catalyzed isomerization of **2** with t-BuOK/DMSO,[11] following the procedure described for **1**.

Irradiation of **2** at −50 °C in pentane resulted in only slight changes in the product distribution. Similarly, irradiation in methanol, which might have trapped vinylcarbene intermediates, gave little change in products. No evidence for methanol adducts was observed.

Independent Generation of Potential Vinylcarbene Intermediates. 3-Methylcyclonon-2-enylidene (**15**) was considered as a potential intermediate in reactions of **2**.[2] This vinylcarbene may arise from an excited-state 1,2-shift of the allenyl hydrogen. To investigate this question, carbene **15** was independently generated, via the method described in our previous studies.[2,3]

3-Methylcyclononenone (**13**) was prepared (Scheme II) by the general transposition method of Dauben and Michno.[12] Treatment of tosylhydrazone **14** with sodium methoxide, followed by Pyrex-filtered photolysis, give an 82% yield of five isomeric (GC–MS) hydrocarbons in the percentages shown in Scheme II. These were isolated by preparative GLC. *cis,trans*-Diene **16** was characterized by its spectral data. The trans configuration about an unsubstituted double bond was indicated by a 16.3-Hz coupling constant. Brief irradiation of **16** afforded isomer **11**.

The behavior of 3-methylcyclonon-2-enylidene (**15**) thus appears to be similar to that of the parent vinylcarbene, cyclonon-2-enylidene.[2] Ring closure to afford cyclopropene products is a major process in each vinylcarbene. Additionally, the exclusive cis stereoselectivity observed in the formation of transannular insertion products (**5** and **6**) again accords with reaction from a singlet vinylcarbene. Both *cis,cis*- and *cis,trans*-1,3-dienes result from each vinylcarbene; however, methyl substitution in **15** allows some interesting insight. The *cis,cis*-1,3-cyclononadiene observed in the reaction of **15** is methyl substituted solely in the 1-position, while the *cis,trans*-1,3-cyclononadiene is methyl substituted exclusively in the 2-position. This demonstrates that the *cis,cis*-diene arises via a 1,2-hydrogen shift, while the *cis,trans*-diene arises via a 1,4-hydrogen shift. Examination of molecular models indicates

(7) Allene **2** has been previously described: Moorthy, S. N.; Vaidyanathaswamy, R.; Devaprabhakara, D. *Synthesis* **1975**, 194.

(8) Photoreactions of dienes **10** and **11** were briefly investigated. Irradiation of **10** yielded a mixture of **11** (major product at low conversion), *trans,cis*-1-methyl-1,3-cyclononadiene, and *cis,cis*-5-methyl-1,3-cyclononadiene. Irradiation of **11** yielded predominantly products of electrocyclization.

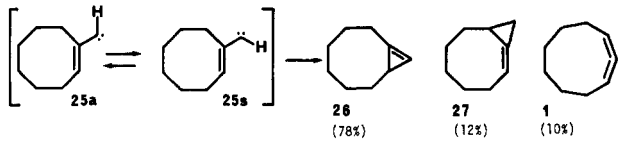
(9) Bicyclics **5** and **6** have been reported previously. **5**: Wolinsky, J.; Clark, G. W.; Thorstensen, P. C. *J. Org. Chem.* **1976**, *41*, 745. **6**: Macdonald, T. L.; Mahlingam, S. *Tetrahedron Lett.* **1981**, 2077.

(10) Brun, P.; Casanova, J.; Hatem, J. *Bull. Soc. Chim. Fr.* **1977**, 521.

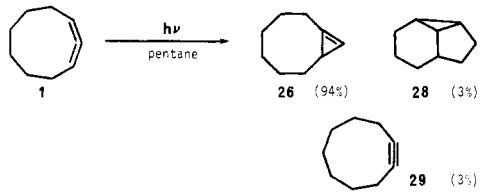
(11) Vaidyanathaswamy, R.; Devaprabhakara, D. *Indian J. Chem.* **1975**, *13*, 873.

(12) Dauben, W. G.; Michno, D. M. *J. Org. Chem.* **1977**, *42*, 682.

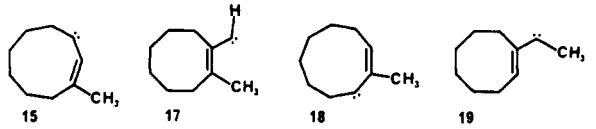
Scheme IV



Scheme V



that the favored conformations for each process may dictate the resultant stereochemistry.



Other 1,2-alkyl shifts in singlet excited **2** could lead to carbenes **17–19**. Although we view these as less likely intermediates, the behavior of **19** was studied since it was expected to afford isomeric cyclopropene **23**; this is also a potential product of **18**. Generation of **19** by the method shown in Scheme III gives nearly pure **23** (50% yield). Spectral data for **23** compared favorably with those reported; this cyclopropene has been previously prepared by another route.[13] Subsequent GLC analyses showed that cyclopropene **23** was undetectable among the photoproducts of **2**.

The behavior of carbene **19** is noteworthy for two reasons. First, the expected 1,2-hydrogen shift to **24** is a very minor process. Second, by comparison to the unsubstituted analogue **25** (Scheme IV)[2] cyclopropene formation is remarkably clean, and no product analogous to **27** is formed. This may be due to a change in the population of syn and anti geometric isomers of the vinylcarbene, which should be precursors to specific products. In **19**, the anti isomer **19a** should be slightly more stable than syn.

Triplet Photochemistry of 2. The triplet photoreactions of allene **2** did not differ significantly from those of **1**.[1,2] Vapor-phase irradiation of **2** with benzene at 254 nm resulted in two predominant products (eq 1), identified as

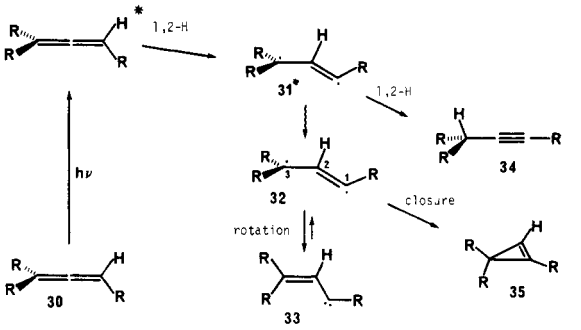
$$2 \xrightarrow[\text{benzene vapor 254 nm}]{h\nu} \text{7 (46\%) + 8 (41\%) + other minor products} \quad (1)$$

2- and 9-methyltricyclo[4.3.0.0^{2,9}]nonanes (**7** and **8**). Confident structure assignment was made by comparison to the 300-MHz ^{1}H NMR spectrum of the parent structure. At least five minor products (total 13%) were observed but were not isolated in sufficient quantities for complete characterization.

Discussion

Excited state 1,2 and 1,3 group migrations are common reactions of allenes.[2-6] In the case of 1,2-cyclononadiene (**1**) we have found evidence for dominant hydrogen migration[2] which yields predominantly **28** (Scheme V). Independent generation of cyclonon-2-enylidene gave 1,3-cyclononadiene and transannular insertion products, which were not observed as primary photoproducts of **1**. This

Scheme VI



led to the conclusion that **1** rearranged to **28** by a concerted [$_\sigma$2$_a$ + $_\pi$2$_a$] mechanism. Similar results were obtained for **3**.[3] In the present study, we find further evidence for migration of hydrogen, rather than possible alkyl substituents; however, *the concerted photorearrangement mechanism appears no longer to be operative.* This is shown by the correspondence between products from irradiation of **2** and the behavior of vinylcarbene **15**. This change in mechanism due to methyl substitution is further evidence of the relationship between concerted and vinylcarbene routes. According to the model for these rearrangements which we previously proposed,[2,5] excited-state hydrogen migration (Scheme VI) leads to a pericyclic minimum at a geometry similar to vinylbiradical **32**.[14] Crossing back to the ground-state surface and in-plane closure give the cyclopropene. Alternatively, rotation about the C2–C3 bond leads to a vinylcarbene, a route favored for phenylallenes.[5,6] One simple explanation for the observed change in mechanism in **2**, relative to **1**, is the anticipated additional stability afforded the vinylcarbene by the C3 methyl substituent. Thus, rotation, rather than closure, is favored as the molecule crosses to the ground-state potential surface.

Alkyl substitution also favors alkyne formation (24% in **2** vs 3% for **1**). We have suggested that alkynes arise from a second excited state hydrogen shift but can see no obvious reason for the change in product distribution due to methyl substitution.

Triplet reactions of allene **2** show little regioselectivity, as might be expected for nearly symmetrical planar allene or cyclopropylidene intermediates. This does not permit distinction between planar allene and cyclopropylidene intermediates.[2]

In summary, alkyl substitution has a surprisingly significant effect on the singlet photoreactions of 1,2-cyclononadiene, but not vapor-phase triplet chemistry. The singlet product distribution is shifted from an apparently concerted mechanism toward one which indicates a vinylcarbene intermediate.

Experimental Section

General. All NMR spectra were measured with $CDCl_3$ as solvent and TMS as reference. Analytical and gas chromatographic separations employed the following columns: (A) 25-m Carbowax 20 M capillary at 60 °C; (B) 25-m DMS capillary at 100 °C; (C) 10 ft × $^1/_8$ in. 10% Carbowax 20 M (glass) at 100 °C; (D) 6 ft × $^1/_8$ in. 15% FFAP at 100 °C; (E) 10 ft × $^1/_4$ in. Carbowax 20 M (glass) at 100 °C; (F) 10 ft × $^3/_8$ in. 10% SE-30 at 60 °C.

Photochemical experiments were conducted as previously described.[2]

1-Methyl-1,2-cyclononadiene (2). This was prepared by the method described for **1**. Treatment of 1-methyl-9,9-dibromobicyclo[6.1.0]nonane with methyllithium at −30 °C, followed by

(13) Suda, M. *Tetrahedron Lett.* **1980**, *21*, 4355.

(14) The existence of a pericyclic minimum is expected for a concerted [$_\sigma$2$_a$ + $_\pi$2$_a$] reaction and is supported by ab initio calculations.

standard workup, gave **2** (94% yield, 98% pure) as a colorless oil: bp 66–69 °C at 7 Torr (lit.[7] bp 66–67 °C at 16 Torr); IR ($CHCl_3$) 2100 cm^{-1}; ^1H NMR (300 MHz) δ 5.17 (br s, 1 H), 2.35–2.10 (m, 2 H), 1.82–1.73 (m, 1 H), 1.69 (d, J = 2.8 Hz, 3 H), 1.65–1.45 (m, 7 H), 1.45–1.25 (m, 2 H).

Direct Irradiation of 1-Methyl-1,2-cyclononadiene (2) in Pentane. A nitrogen-degassed solution of 231 mg of 1-methyl-1,2-cyclononadiene (**2**) in 300 mL of pentane was irradiated for 5 h with a Vycor-filtered 450-W mercury lamp. Progress of reaction was monitored by GLC analysis (column B) of aliquots at regular intervals. The solution was concentrated under reduced pressure at 0 °C to give 246 mg of a clear oil. GLC (column C), capillary GLC (column B), and 300-MHz ^1H NMR analysis indicated 15% conversion to 10 products. These were isolated on a preparative scale (columns E and F), and the following were characterized by the identity of their capillary GLC (column B and column A) retention times and 300-MHz ^1H NMR spectra with those of authentic samples. (GLC retention times listed are those observed on column B.) 8-Methylbicyclo[6.1.0]non-1(9)-ene (**4**, 21%, t_R 6.73 min) [^1H NMR (300 MHz, $CDCl_3$) δ 6.54 (br s, 1 H), 2.63 (dt, J = 14.1 Hz, J = 4.6 Hz, 1 H), 2.29 (dddd, J = 14.1, 10.0, 5.3, 1.8 Hz, 1 H), 1.88–1.76 (m, 1 H), 1.63–1.23 (m, 8 H), 1.13 (s, 3 H), 1.10–0.96 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 132.2, 107.3, 37.4, 30.5, 27.1, 26.2, 25.8, 25.7, 25.0, 20.7; IR (GC–IR) 2935, 2866, 1771, 1454, 1373 cm^{-1}; HRMS 136.1255 (calcd 136.1252)]; *cis*-8-methylbicyclo[4.3.0]non-7-ene (**5**, 31%, t_R 7.21 min); 9-methyltricyclo[4.3.0.$0^{2,9}$]nonane (**7**, 2%, t_R 7.53 min); 2-methyltricyclo[4.3.0.$0^{2,9}$]nonane (**8**, 2% t_R 7.78 min); *cis,cis*-2-methyl-1,3-cyclononadiene (**11**, 3%, t_R, 7.90 min); *cis*-3-methylbicyclo[4.3.0]non-2-ene (**6**, 16%, t_R 8.46 min); 3-methylcyclononyne (**9**, 19%). [^1H NMR (300 MHz, $CDCl_3$) δ 2.55–2.45 (m, 1 H), 2.18–2.12 (m, 2 H), 1.83–1.73 (m, 1 H), 1.73–1.32 (m, 9 H), 1.07 (d, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 92.1, 86.6, 36.5, 30.3, 27.2, 26.9, 25.6, 24.0, 20.4, 19.2; IR (neat) 2964, 2930, 2860, 2231, 1456, 1373 cm^{-1}; HRMS 136.1253 (calcd 136.1252).

***cis*-8-Methylbicyclo[4.3.0]non-7-ene (5).**[9] A solution of *cis*-bicyclo[4.3.0]nonan-8-one (0.50 g, 3.6 mmol) in dry ether was added dropwise to methyllithium (8.0 mmol) at room temperature. Conventional workup afforded *cis*-8-methylbicyclo[4.3.0]nonan-8-ol (0.53 g, 95%) as a clear oil. A solution of the crude alcohol (0.47 g, 3.0 mmol) in a 3 mL of dry DMSO was heated to 160 °C and stirred for 24 h. After cooling, the mixture was poured into water (25 mL) and extracted with pentane (25 mL). The extract was washed with water, dried over magnesium sulfate, filtered through neutral alumina, and concentrated to give **5** (0.25 g, 61%) as a clear oil: ^1H NMR (300 MHz, $CDCl_3$) δ 5.25 (narrow m, 1 H), 2.57–2.47 (m, 1 H), 2.25–2.13 (m, 2 H), 1.91 (dd, 1 H), 1.71 (s, 3 H), 1.65–1.20 (m, 8 H).

***cis*-3-Methylbicyclo[4.3.0]non-2-ene (6).**[9] Reaction of *cis*-bicyclo[4.3.0]nonan-3-one (0.50 g, 3.6 mmol) with methyllithium (7.2 mmol) as described above gave the alcohol (0.54 g, 3.5 mmol, 97%) as a clear oil. The crude product (0.51 g, 3.31 mmol) in 5 mL of dry DMSO was heated to 160 °C and stirred for 24 h. The reaction was worked up as above to give the product (0.28 g, 2.1 mmol, 63%) as a clear oil. Capillary GLC (column B) analysis indicated two components, which were separated on a preparative scale (column E at 75 °C) and identified as follows. *cis*-3-Methylbicyclo[4.3.0]non-2-ene (**6**, 81%): ^1H NMR (300 MHz, $CDCl_3$) δ 5.34 (narrow m, 1 H), 2.38–2.27 (m, 1 H), 2.07–1.93 (m, 1 H), 1.86 (t, J = 6.1 Hz, 2 H), 1.83–1.22 (m, 8 H), 1.65 (s, 3 H). *cis*-3-Methylbicyclo[4.3.0]non-3-ene (19%): ^1H NMR (300 MHz, $CDCl_3$) δ 5.33 (br s, 1 H), 2.15–1.87 (m, 4 H), 1.87–1.55 (m, 6 H), 1.65 (s, 3 H), 1.45–1.30 (m, 2 H).

Base-Catalyzed Isomerization of 1-Methyl-1,2-cyclononadiene. 1-Methyl-1,2-cyclononadiene (0.52 g, 3.8 mmol) was added to potassium *tert*-butoxide (1.0 g, 8.9 mmol) in 5 mL of dry DMSO. The mixture was stirred for 21 h, poured into 20 mL of water, and extracted with pentane (30 mL). The extract was washed with water, dried, filtered through neutral alumina, and concentrated under reduced pressure at 0 °C to afford 0.403 g (78%) of a clear oil. GLC analysis (column C) indicated complete conversion to four products. The four components were isolated on a preparative scale (column E) and identified as follows. *cis,cis*-2-Methyl-1,3-cyclononadiene (28%): ^1H NMR (300 MHz) δ 5.82 (d, J = 10.7 Hz, 1 H), 5.61 (dt, J = 10.7 Hz, J = 8.3 Hz, 1 H), 5.37 (t, J = 8.3 Hz, 1 H), 2.09–2.00 (m, 4 H), 1.70 (s, 3 H), 1.65–1.55 (m, 2 H), 1.47–1.37 (m, 4 H). *cis,cis*-1-Methyl-1,3-cyclononadiene (**10**, 53%): ^1H NMR (300 MHz) δ 5.86 (d, J = 10.7 Hz, 1 H), 5.66 (dt, J = 10.7, 8.3 Hz, 1 H), 5.59 (s, 1 H), 2.13–2.04 (m, 4 H), 1.74 (s, 3 H), 1.60–1.40 (m, 6 H). Minor products were characterized by NMR. *cis,cis*-2-Methyl-1,4-cyclononadiene (10%): ^1H NMR (300 MHz) δ 5.68 (dt, J = 10.4 Hz, J = 8.1 Hz, 1 H), 5.53 (dt, J = 10.4 Hz, J = 8.4 Hz, 1 H), 5.20 (t, J = 8.3 Hz, 1 H), 2.81 (d, J = 8.1 Hz, 2 H), 2.26–2.14 (m, 4 H), 1.73 (s, 3 H), 1.55–1.45 (m, 4 H). *cis,cis*-1-Methyl-1,4-cyclononadiene (9%): ^1H NMR (300 MHz) δ 5.60–5.44 (m, 2 H), 5.27 (t, J = 8.3 Hz, 1 H), 2.78 (t, J = 8.0 Hz, 2 H), 2.28–2.15 (m, 4 H), 1.67 (s, 3 H), 1.65–1.45 (m, 4 H).

1-Acetylcyclooctene (21). This was prepared in 47% yield by treatment of 1-bromocyclooctene with t-BuLi at −78 °C followed by addition of *N,N*-dimethylacetamide, and standard workup: bp 90–100 °C at 5 Torr (lit.[15] bp 105–107 °C at 11 Torr); ^1H NMR (300 MHz, $CDCl_3$) δ 6.87 (t, J = 8.3 Hz, 1 H), 2.46–2.42 (m, 2 H), 2.38–2.30 (m, 2 H), 2.31 (s, 3 H), 1.67–1.57 (m, 2 H), 1.57–1.38 (m, 6 H).

1-Acetylcyclooctene Tosylhydrazone (22). 1-Acetylcyclooctene (1.50 g, 9.85 mmol) was added to a stirring slurry of tosylhydrazide (1.84 g, 9.88 mmol) in 10 mL of methanol. The mixture was stirred at room temperature for 60 min and cooled to 0 °C, and the crystals were collected and washed with cold methanol. The filtrate (ca. 50 mL) was cooled at 0 °C, water (ca. 10 mL) was added to induce crystallization, and a second crop of crystals were collected and washed with cold 75% aqueous methanol. The crystals were warmed and dried on a vacuum line overnight. The tosylhydrazone (2.70 g, 86%) was obtained as white crystals: mp 118–119 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, J = 8.2 Hz, 2 H), 7.52 (br s, 1 H), 7.29 (d, J = 8.2 Hz, 2 H), 6.11 (t, J = 8.2 Hz, 1 H), 2.52–2.48 (m, 2 H), 2.42 (s, 3 H), 2.28–2.21 (m, 2 H), 1.87 (s, 3 H), 1.57–1.28 (m, 8 H); IR (KBr) 3230, 3040, 2930, 2860, 1620, 1600, 1450, 1390, 1345, 1165, 920 cm^{-1}. Anal. Calcd for $C_{17}H_{24}N_2O_2S$: C, 63.72; H, 7.55; N, 8.74. Found: C, 63.62; H, 7.54; N, 8.91.

Photolysis of the Sodium Salt of 1-Acetylcyclooctene Tosylhydrazone (22). 1-Acetylcyclooctene tosylhydrazone (1.00 g, 3.12 mmol) and sodium methoxide (0.80 g 15 mmol) in 300 mL of dry, degassed THF at −15 °C was irradiated through Pyrex for 1 h. The reaction was poured into pentane (200 mL), and the pentane was washed with water (6 × 400 mL), dried, and concentrated at 0 °C to give 0.218 g (51%) of hydrocarbon product as a clear oil. Capillary GLC (column A) and high-field NMR analysis indicated three components identified as follows: 9-methylbicyclo[6.1.0]non-1(9)-ene (**23**, 98%) [^1H NMR (300 MHz) δ 2.61 (ddd, J = 14.4 Hz, J = 5.7 Hz, J = 3.9 Hz, 1 H), 2.23–2.10 (m, 1 H), 1.97 (d, J = 2.0 Hz, 3 H), 1.88–1.76 (m, 1 H), 1.62–1.12 (m, 10 H); 1-methyl-1,2-cyclononadiene (**2**, 1%); 1-vinylcyclooctene (**24**, 1%) [^1H NMR (300 MHz, $CDCl_3$) δ 6.29 (dd, J = 17.4 Hz, J = 10.7 Hz, 1 H), 5.71 (t, J = 8.3 Hz, 1 H), 5.11 (d, J = 17.4 Hz, 1 H), 4.91 (d, J = 10.7 Hz, 1 H)]. An authentic sample of **24** was prepared for comparison.

3-Methylcyclonon-2-en-1-one (13). 3-Methylcyclonon-2-en-1-one (**13**) was prepared by the general procedure of Dauben and Michno.[12] Methyllithium (27 mmol) was added dropwise to cyclonon-2-en-1-one (3.07 g, 22.2 mmol) in 100 mL of dry ether at −78 °C. The mixture was allowed to warm to room temperature and stir for 2 h, followed by standard workup.

The crude 1-methylcyclonon-2-en-1-ol in 20 mL of methylene chloride was added to a stirring slurry of pyridinium chlorochromate (9.6 g, 44.5 mmol) in 60 mL of methylene chloride, and the mixture was stirred at room temperature for 2 h. After dilution with 100 mL of ether, the solution was decanted from the black residue, and the residue was washed with ether. The product solution was washed with 5% aqueous sodium hydroxide (2 × 200 mL), water (200 mL), 5% aqueous hydrochloric acid (2 × 200 mL), water (200 mL), saturated aqueous sodium bicarbonate (200 mL), and water (200 mL). The solution was then dried over sodium sulfate, filtered, and concentrated under reduced pressure. Capillary GLC (column B at 150 °C) analysis indicated one major and six minor components. The crude material was chromatographed over silica gel (3 cm × 60 cm column), eluting with 10%

(15) Olah, G. A.; Fung, A. P. *Synthesis* **1981**, 473.

ether/hexanes in 150-mL fractions. Fractions 5–7 contained material with >95% purity by capillary GLC analysis. Concentration under reduced pressure and distillation gave 3-methylcyclonon-2-en-1-one (0.68 g, 20%) as a clear oil: bp 103–105 °C at 4.8 Torr; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.00 (s, 1 H), 2.71–2.67 (m, 2 H), 2.61–2.57 (m, 2 H), 1.94 (t, J = 1.3 Hz, 3 H), 1.87–1.77 (m, 2 H), 1.65–1.54 (m, 4 H), 1.46–1.36 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 205.6, 153.4, 130.5, 40.9, 31.0, 28.7, 28.4, 27.2, 26.7, 24.3; IR (neat) 2920, 2860, 1640, 1470, 1440, 1225, 1165 cm^{-1}; HRMS (M^+) 152.1198 (calculated 152.1201).

3-Methylcyclonon-2-en-1-one Tosylhydrazone (14). 3-Methylcyclonon-2-en-1-one (0.50 g, 3.3 mmol) was added to a stirring suspension of tosylhydrazide (0.61 g, 3.3 mmol) in 10 mL of benzene. The mixture was stirred at room temperature for 60 min and cooled to 0 °C, and pentane was added to induce crystallization. The crystals were collected, washed with pentane, and dried to give the desired tosylhydrazone (0.57 g, 1.8 mmol, 55%) as off-white crystals: mp 108–112 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 2 H), 7.62 (br s, 1 H), 7.29 (d, J = 8.2 Hz, 2 H), 5.35 (d, J = 1.2 Hz, 1 H), 2.42 (s, 3 H), 2.36–2.31 (m, 2 H), 1.77 (d, J = 1.2 Hz, 3 H), 1.81–1.74 (m, 1 H), 1.65–1.55 (m, 3 H), 1.45–1.25 (m, 6 H); IR (KBr) 3195, 2920, 2850, 1645, 1595, 1440, 1380, 1330, 1155, 1035 cm^{-1}. Anal. Calcd for $C_{17}H_{24}N_2O_2S$: C, 63.72; H, 7.55; N, 8.74. Found: C, 63.44; H, 7.71; N, 8.85.

Photolysis of the Sodium Salt of 3-Methylcyclonon-2-en-1-one Tosylhydrazone (14). Reaction of 3-methylcyclonon-2-en-1-one tosylhydrazone (**14**, 250 mg, 0.78 mmol) as described above gave 87 mg (0.64 mmol, 82%) of hydrocarbon product as a clear oil. Capillary GLC (column B) analysis indicated five components. GC–MS showed all products to be isomeric. These were isolated on a preparative scale and were characterized by the identity of their capillary GLC (column B) retention times and 300-MHz ^{1}H NMR spectra with those of authentic samples, with the exception of *cis,trans*-2-methyl-1,3-cyclononadiene. *cis,trans*-2-Methyl-1,3-cyclononadiene was characterized by its 300-MHz ^{1}H NMR spectrum, and by its facile photoisomerization to *cis,cis*-2-methyl-1,3-cyclononadiene. Products were identified as follows: 8-methylbicyclo[6.1.0]non-1(9)-ene (**4**, 30%); *cis*-8-methylbicyclo[4.3.0]non-7-ene (**5**, 9%); *cis*-3-methylbicyclo[4.3.0]non-2-ene (**6**, 36%); *cis,cis*-1-methyl-1,3-cyclononadiene (**10**, 19%); *cis,trans*-2-methyl-1,3-cyclononadiene (**16**, 5%) [^{1}H NMR (300 MHz, $CDCl_3$) δ 5.69 (d, J = 16.3 Hz, 1 H), 5.56–5.45 (m, 2 H), 2.40–2.15 (m, 2 H), 2.15–1.90 (m, 2 H), 1.75–1.25 (m, 6 H), 1.78 (s, 3 H)].

Vapor-Phase Benzene-Sensitized Irradiation of 1-Methyl-1,2-cyclononadiene. 1-Methyl-1,2-cyclononadiene (350 mg) and benzene (500 μL) were placed into a 3.7-L Vycor tube, the system was degassed as described previously,[2] and the vapor-phase mixture was irradiated for 5 days in a Rayonet photoreactor fitted with 254-nm lamps. The reaction vessel was then cooled on the bottom to −78 °C and vented to nitrogen, and the product was collected in pentane. The pentane solution was filtered through neutral alumina and was concentrated under reduced pressure at 0 °C to give 294 mg of a clear oil. Capillary GLC (column A) analysis indicated 97% conversion to six major products. These were isolated on a preparative scale (column E at 80 °C), and the major products were identified as follows: 9-methyltricyclo[4.3.0.0^{2,9}]nonane (**7**, 46%, t_R 3.91 min) [^{1}H NMR (300 MHz, $CDCl_3$) δ 2.50–2.42 (m, 1 H), 2.30–2.15 (m, 1 H), 1.88–1.78 (m, 3 H), 1.62–1.54 (m, 1 H), 1.41–1.20 (m, 6 H), 1.11 (s, 3 H), 0.70–0.64 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 38.2, 33.8, 32.8, 31.3, 28.6, 28.0, 24.5, 23.9, 19.2, 17.2; IR (neat) 3020, 2990, 2940, 2870, 1480, 1450 cm^{-1}; HRMS (M^+) 136.1249 (calculated 136.1252)]; 2-methyltricyclo[4.3.0.0^{2,9}]nonane (**8**, 41% t_R 4.20 min) [^{1}H NMR (300 MHz, $CDCl_3$) δ 2.46–2.40 (m, 1 H), 2.23–2.08 (m, 1 H), 1.94–1.53 (m, 4 H), 1.47–1.25 (m, 6 H), 1.08 (td, J = 7.4 Hz, J = 2.0 Hz, 1 H), 0.90 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 40.1, 33.8, 33.4, 31.3, 28.8, 28.7, 27.1, 26.9, 21.1, 18.3; IR (neat) 3020, 2940, 2880, 1480, 1450 cm^{-1}; HRMS (M^+) 136.1254 (calculated 136.1252)]. Minor products (five in 2–4% yield each) were incompletely characterized.

In other experiments conducted at lower conversion (18–40%), the ratio of photoproducts remained unchanged.

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Registry No. **2**, 42915-27-5; **4**, 124267-67-0; **5**, 57497-08-2; **6**, 79884-82-5; **7**, 124267-68-1; **8**, 124267-69-2; **9**, 124267-70-5; **10**, 124267-74-9; **11**, 124267-72-7; **13**, 124267-77-2; **14**, 124267-78-3; **16**, 124267-80-7; **20**, 4103-11-1; **21**, 17339-74-1; **22**, 124286-31-3; **23**, 77197-66-1; **24**, 80304-18-3; *cis*-bicyclo[4.3.0]nonan-8-one, 5689-04-3; *cis*-8-methylbicyclo[4.3.0]nonan-8-ol, 124267-71-6; *cis*-bicyclo[4.3.0]nonan-3-one, 4668-91-1; 1-methyl-9,9-dibromobicyclo[6.1.0]nonane, 70239-06-4; bicyclo[4.3.0]nonan-3-ol, 3716-38-9; *cis*-3-methylbicyclo[4.3.0]non-3-ene, 124267-73-8; (*Z,Z*)-2-methyl-1,4-cyclononadiene, 124267-75-0; (*Z,Z*)-1-methyl-1,4-cyclononadiene, 124267-76-1; 2-cyclononen-1-one, 1195-60-4; 1-methylcyclonon-2-en-1-ol, 124267-79-4.

Structural Effects on the Disproportionation Equilibrium of Tethered Tetraphenylethylene Radical Anions

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The electrochemistry of four bis[*n*.1]metacyclophanylidenes has been studied by cyclic and differential pulse voltammetric methods. The potential differences between the first and second reduction steps for these cyclophanes depend on the length of the hydrocarbon tethers and therefore on the magnitude of phenyl ring torsion. This behavior can be correlated with the photophysical properties of these compounds, on the basis that the lowest singlet excited state is isolobal with the dianion. Since the potential difference between the first and second reduction steps is related to the disproportionation equilibrium constant, phenyl ring torsion, rather than olefinic torsion, may play a major role in determining the ion pairing and electrochemical properties of tetraphenylethylenes.

Introduction

Recently we have demonstrated that phenyl ring torsion plays a dominant role in the partitioning among tetraphenylethylene (TPE) singlet excited-state relaxation pathways.[1] For example, a strong increase in fluorescence quantum yield is observed if phenyl ring torsion is restricted by hydrocarbon tethers connecting geminal phenyl

(1) (a) Shultz, D. A.; Fox, M. A. *Tetrahedron Lett.* **1988**, *29*, 4377. (b) Shultz, D. A.; Fox, M. A. *J. Am. Chem. Soc.* **1989**, *111*, 6311.

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